

***ELECTROPHORETIC METHOD FOR THE PRODUCTION OF CERAMIC  
STRUCTURES***

- [0001] The invention relates to a method for producing ceramic structures (for example layers, filters, or micro-structures), as well as to structures and gradient structures produced with this method.
- [0002] Ceramic (micro-) structures, ceramic layers, and two-dimensional structures such as tiles, substrates, or filters are gaining in importance in many fields of technology. In particular, this is true for the so-called structural ceramics such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , mullite,  $\text{SiC}$ ,  $\text{Si}_3\text{N}_4$ , the functional ceramics such as  $\text{BaTiO}_3$  or PZT (lead-zirconate-titanate), and the so-called bio-ceramics, such as hydroxyl apatite  $\text{Ca}(\text{OH})(\text{PO}_4)_3$ , but also for mineral glass materials. Depending on the form, size and area of use for the parts or layers to be produced, the following production methods are used: dry pressing, powder-technological injection molding, hot molding, slip casting, foil casting, electrophoretic deposition from powder suspensions, and other methods which are followed by a sintering step.
- [0003] All known methods have in common that so-called feedstocks are used for the molding, wherein these feedstocks consist of ceramic powders and binders, dispersing agents, as well as slip additives for improving the workability. With the pressing methods, only small percentages by volume of these additives are added to the powders. With the injection molding, hot molding, slip molding, and foil casting methods, on the other hand, much higher percentages by volume of binders, dispersing

agents, slip agents, polymers, waxes and suspension liquids such as water and alcohol are added. With these methods, the powder share ranges from 30 to 70 percentages by volume. For the electrophoretic deposition from watery or alcoholic suspensions, the percentage by volume of ceramic powder can range from approximately 5% to 50%.

[0004] All methods furthermore have in common that the distribution of particles in the powder for the so-called green product is approximately the same as in the starting powder, the slip, the feedstock, or the suspension. In general, powders are used which have a relatively broad distribution in the form of so-called mono-modal powders, wherein these frequently follow normal distributions, logarithmic normal distributions, or so-called Rosin-Rammler distributions. In part, powders are also used which are present in the form of complex multi-modal distributions.

[0005] The roughness of the produced parts and layers, as well as their pore sizes and to some degree also their structure following the sintering, are influenced by the distribution of particle sizes. For example, the rough components of the powder that is used determine the surface roughness. The distribution of pore sizes in the filter membranes is correlated to the particle size: the larger the powder particles, the larger the pores that develop. For that reason, only particles below a specific size, e.g. 500nm, can therefore be used with traditional production methods to achieve, for example, especially smooth layers or micro-structures or to obtain extremely small pore sizes. For this, the powders must first be fractionated and graded in a complicated manner before the starting feedstock is produced, for example by means

of screening or wind-sifting, and only the desired powder fraction should be introduced into the feedstock.

[0006] For cost reasons, these additional and very involved processing steps are out of the question for most applications. Particularly smooth layers with peak-to-valley heights below 1  $\mu\text{m}$  and micro-structures with surface details in the  $\mu\text{m}$  range can therefore not be produced by using traditional, commercially available powders with powder sizes that are generally in the range above 1  $\mu\text{m}$ .

[0007] Starting from this point, it is the object of the present invention to provide methods for producing ceramic structures which are not subject to the aforementioned disadvantages and restrictions.

[0008] This object is solved with the method as defined in claim 1. The dependent claims describe advantageous embodiments of the invention.

[0009] The method according to the invention is based on combining the electrophoretic deposition and the sedimentation due to gravitational forces and/or centrifugal forces. The electrophoretic deposition of ceramic particles from particle suspensions as a method for producing ceramic layers is known (Heavens, S.N.: *Electrophoretic Deposition as a Processing Route for Ceramics*; in Binner, J. (Ed.), *Advanced Ceramic Processing and Technology*, Vol. 1, Noyes Publ., Park Ridge, N.J. U.S.). Attempts have recently been made to use this technique also for realizing ceramic micro-structures (Both, H. von; Hausselt, J.: *1<sup>st</sup> Intern. Conf. on Electrophoretic Deposition*, Banff, Canada, 2002). For this, an electric field is applied between two electrodes submerged in the powder suspension, causing a flow of charged particles to

move toward one of the two electrodes and causing the particles to be deposited thereon.

[00010] The principles of electrophoresis have long been known. Corresponding theoretical descriptions disclose that in the size range for ceramic powders used for technical applications, meaning in the range between 10nm and 100µm, the electrophoretic mobility of the powder particles for the most part does not depend on their size (Nitzsche, R.; Simon, F.: "TECHNISCHES MESSEN" [Technical Measuring] Volume 64, pages 106-113, 1997). All particle sizes occurring in the suspension should therefore be deposited with substantially the same speed on the electrically conductive substrate. The deposited layers consequently should have the same distribution of particle sizes as the suspension, albeit packed with substantially higher density.

[00011] Our own measurements confirm that the migration rate  $v_E$  in the electric field  $E$  depends not only on the suspension medium (e.g. watery or alcoholic), the chemical composition of the powder (e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ), and the added dispersing and binding agents, but can also depend to a small degree on the existing particle size. Depending on the system, it is possible to observe different, but always small, dependencies of the migration rate on the particle size.

[00012] Experiments with alcoholic  $\text{Al}_2\text{O}_3$  suspensions have shown that smaller particles are deposited slightly faster than larger ones, but that this effect is not sufficient for a technical use, for example for the electrophoretic in-situ-fractionizing. For the

electrophoretic deposition, the mobility  $\mu$  and the migration rate  $v_E$  consequently depend on the particle size (radius  $r$ ) in the electric field  $E$ , wherein:

$$dv_E/dr \leq 0 \quad (1a)$$

and, owing to  $v_E = \mu E$

$$d\mu/dr \leq 0 \quad (1b)$$

applies.

[00013] In watery suspensions with spherical SiO<sub>2</sub> particles having diameters between 200nm and 1200nm, on the other hand, larger particles will be deposited slightly faster than finer particles. Thus, for the electrophoretic deposition, the mobility  $\mu$  and the migrating rate  $v_E$  depend on the particle size (radius  $r$ ) in the electrical field  $E$ , wherein:

$$dv_E/dr \geq 0 \quad (1c)$$

and, owing to  $v_E = \mu E$

$$d\mu/dr \geq 0 \quad (1d)$$

applies.

[00014] For a number of applications, it is desirable to have a deposition of only specific fractions, such as the share of fine particles in a predetermined distribution of particle sizes. For the above-described reasons this cannot be achieved with the electrophoretic deposition according to the prior art. The known technique of electrophoretic deposition from powder suspension furthermore cannot be used for applications using a single deposition and without changing the powder suspension,

for which initially only rough particles are deposited and, with progressing time and layer thickness, smaller powder particles are deposited gradually or continuously.

[00015] According to the invention, a field which causes a particle speed that depends on the particle size is superimposed on the electrical field which causes a particle speed that is mostly independent of the particle size in the direction of the electrical field. For this type of application, the deposit by sedimentation which depends on the particle size is suitable, either in a constant, locality-independent gravitation field (gravity sedimentation) or in a variable and locality-dependent gravitation field (centrifuging).

This is in contrast to the standard electrophoresis where the effective gravitational force resulting from the earth's gravitational field, which is undesirable for specific applications, is eliminated with the aid of suitable measures such as a special arrangement of the electrodes and especially by stirring the suspension.

[00016] For individual spherical particles with a radius  $r$  and a density  $p$ , which are dispersed (suspended) in a liquid with the density  $p_F$  and the viscosity  $\eta$ , this results in a sedimentation rate  $v$  based on the Stokes law, under the effect of an acceleration  $b$ :

$$6\pi\eta r v = (4\pi / 3) r^3 (p - p_F) b \quad (2)$$

[00017] The sedimentation rate  $v$  is therefore proportional to  $r^2$  if the viscosity  $\eta$  is constant. Even in cases of deviations from the equation 2 because of particle shapes which generally differ from the spherical form and at higher concentrations for the suspensions, the qualitative relation remains in place, which indicates that the

sedimentation rate increases with increasing particle size and increasing difference in the density values. In any case, the following applies:

$$dv/dr > 0. \quad (3)$$

[00018] If the direction of the migration rate in the electric field is counter to the sedimentation rate in the gravitational field, a critical particle size  $r_c$  is obtained for each electrical field intensity  $E$  and for each acceleration  $b$  in the gravitational field, wherein the effects of both fields cancel each other out and the particle is suspended. All particles with  $r > r_c$  move in the direction of the gravitational field while all particles with  $r < r_c$  move in the direction of the electrical field. Depending on the selection of the electrical field intensity  $E$  and the acceleration  $b$  (e.g. by varying the speed in a centrifuge), freely selectable fractions of the original distribution of particle sizes can for the most part be deposited on an electrically conductive substrate.

[00019] In general, the angle between the directions of the electrical field and the gravitational field is selected such that a speed component which depends on the particle size can be added or subtracted for a mostly particle-size independent speed distribution in the electric field. The effect of the constant and locality- independent acceleration due to gravity by itself makes it possible to ensure that the share of fine particles in a distribution is advantageously deposited on an electrode by varying the electrical field intensity and the angle between both field directions. The electrical and the gravitational fields are preferably arranged parallel to each other, meaning the

electrodes are positioned substantially perpendicular to the direction of the gravitational field (e.g. horizontally in the gravity field).

[00020] In contrast to the traditional electrophoresis, our invention provides that one fraction of the suspended particles is deposited under the effect of gravity on the upper electrode. The fraction deposited in the form of a ceramic structure generally is distinguished in that its distribution of particle sizes differs from the distribution of particle sizes in the suspension, which is not the case with the standard electrophoresis. Since the finer particles are preferably deposited, the distribution of particle sizes in the ceramic structure has lower values than the distribution of particle sizes in the suspension.

[00021] According to one preferred embodiment of the invention, the distribution of the particle sizes to be deposited can be influenced by freely selecting not only the absolute value, but also the point in time for superimposing the sedimentation by gravity on the electrical field. The respectively desired limit for the deposited size fraction can be adjusted by varying the electrical field intensity.

[00022] A particularly preferred embodiment of the invention is obtained by superimposing a gravitational field with variable absolute value on an electrical field with variable absolute value, as shown in particular with the centrifuging operation where centrifugal forces occur. While activated, the generated gravitational field is directed toward the outside, relative to the axis of rotation of the centrifuge. As a result of this arrangement, the share of micro particles in the suspension is deposited according to the invention in the form of a ceramic layer on the inner electrode.



[00023] The distribution of particle sizes to be deposited can furthermore be influenced by not only selecting the absolute values of the electrical field and the gravitational field of the centrifugal acceleration over broad ranges, but also by freely selecting the points in time when both fields are activated and/or shut down.

[00024] The present invention can furthermore be used for suspensions (dispersions) containing a mixture of different particles. If such particle mixtures differ in their specific electrical charge, their electrophoretic mobility and their electrophoretic deposition rates also differ. Thus, if such particle mixtures differ in their density, their sedimentation rates differ in the gravitational and/or the centrifugal field since in both cases the sedimentation rate according to the equation 2 is proportional to the difference between the density of the particles and the density of the suspension liquid.

[00025] Superimposing a gravitational field on an electrical field therefore permits a far-reaching influencing of the conditions for depositing particle mixtures which differ not only in size, but also in their surface charge and/or density. Furthermore, the method according to the invention can also be used to separate particle mixtures which do not differ in particle size, but in their surface charge and/or density.

[00026] The method according to the invention can be used for creating ceramic structures by means of a multiple and/or continuous variation of the electrical field and/or (in the case of centrifuging) the gravitational field during a deposition, without having to change the powder suspension, wherein the structures have a gradient with respect to their composition and/or pore depth. Ceramic gradient structures of this type are suitable, for example, for use as filter membranes.

[00027] In addition, the method according to the invention is suitable not only for producing layers for which the distribution of particle sizes or, if several different powders are used, composition can be varied widely, but also for separating suspensions with an expanded variation range as compared to the pure deposit by sedimentation or the centrifuging methods.

[00028] The invention is explained further in the following, with the aid of five exemplary embodiments.

#### **Exemplary Embodiment 1:**

[00029] An  $\text{Al}_2\text{O}_3$  layer was produced by superimposing gravitational sedimentation on electrophoretic deposition. Counter electrode and substrate were arranged horizontally, meaning both surfaces of the electrode pair were oriented perpendicular to the direction of the gravitational field. In order to show that increasingly finer particles are deposited by means of superimposed sedimentation, the peak-to-valley height was measured optically with the aid of a surface measuring device (FRT MicroGlider). For a comparison, a layer was deposited for which the deposit by sedimentation was suppressed through stirring, according to prior art, and the electrodes were arranged vertically.

An ethanol  $\text{Al}_2\text{O}_3$  suspension ( $d_{50} = 1300\text{nm}$ ) starting batch was prepared, with 30 percent by volume solid material and a dispersing agent content of 2 percent by mass, relative to the powder mass. The layers were deposited from this suspension under the following conditions (in the case of a horizontal arrangement of the upper electrode):

|                               | without stirring   | with stirring<br>(200 rpm) |
|-------------------------------|--------------------|----------------------------|
| electrode arrangement         | horizontal         | vertical                   |
| current                       | 1000 $\mu$ A       | 100 $\mu$ A                |
| deposition time               | 7 hours 51 minutes | 30 minutes                 |
| average peak-to-valley height | 80nm               | 341nm                      |

[00030] The spacing between electrodes was 13mm. Respectively four profiles were analyzed in one ceramic layer and the average value listed. The result showed a clear reduction in the peak-to-valley height with superimposed sedimentation, respectively determined on the basis of DIN 4678 and/or ISO 4287.

#### **Exemplary Embodiment 2**

[00031] Using different field intensities, Al<sub>2</sub>O<sub>3</sub> layers were produced by superimposing gravitational sedimentation on electrophoretic deposition. Counter electrode and substrate were arranged horizontal, relative to each other. To show that the particles are separated based on their diameter by varying the field intensity during the electrophoretic deposition, the peak-to-valley height was measured optically with the aid of a surface measuring device (FRT MicroGlider).

A batch of an ethanol Al<sub>2</sub>O<sub>3</sub> suspension ( $d_{50} = 1300\text{nm}$ ) was prepared for this, with 5 percent by volume solid material and a dispersing agent content of 2 percent by mass, relative to the powder mass. The layers were deposited from this suspension under the following conditions:

|                               |           |            |
|-------------------------------|-----------|------------|
| field intensity               | 2500 V/m  | 250 V/m    |
| deposition time               | 2 minutes | 30 minutes |
| average peak-to-valley height | 106nm     | 74nm       |

[00032]        Respectively four profiles were analyzed in one layer and the average value listed. Based on DIN 4678 and/or ISO 4287, a higher peak-to-valley height was measured for the layers deposited at higher field intensities. This result confirms the separation of particles based on their diameter.

### **Exemplary Embodiment 3:**

[00033]        A SiO<sub>2</sub> layer was produced by superimposing the gravitational sedimentation on the electrophoretic deposition. Counter electrode and substrate were arranged horizontally. The peak-to-valley height was measured optically with a surface measuring device (FRT MicroGlider) to show that increasingly finer particles are deposited with the aid of sedimentation. For a comparison, an additional layer was deposited for which the sedimentation was suppressed by stirring the suspension, corresponding to the prior art, and for which the electrodes were arranged vertically. A starting batch of ethanol SiO<sub>2</sub> suspension ( $d_{50} = 15\mu\text{m}$ ) was prepared, with 5 percentages by volume solid material and a dispersing agent content of 2 percentages by mass, relative to the powder mass. The layers were deposited from this suspension under the following conditions:

|                                   | without stirring | without stirring | with stirring<br>(200 rpm) |
|-----------------------------------|------------------|------------------|----------------------------|
| electrode<br>arrangement          | horizontal       | horizontal       | vertical                   |
| voltage                           | 50V              | 10V              | 50V                        |
| average peak-<br>to-valley height | 1.20 $\mu$ m     | 0.12 $\mu$ m     | 1.77 $\mu$ m               |

[00034] The spacing between electrodes was 13mm. Respectively four profiles were analyzed in one layer and the average value listed. A clear reduction in the peak-to-valley height resulted for the superimposed sedimentation, detected according to DIN 4678 and/or ISO 4287.

#### **Exemplary Embodiment 4:**

[00035] An Al<sub>2</sub>O<sub>3</sub> layer was produced according to the invention by superimposing the gravitational sedimentation on the electrophoretic deposition. The electrodes were arranged horizontal. The electrophoretic deposition occurred on the upper electrode. An optical laser granulometer was used to determine the distribution of particle sizes in the suspension and in the layer to show that increasingly finer particles are deposited when superimposing the sedimentation rather than suppressing the sedimentation by stirring the suspension.

For this, an ethanol Al<sub>2</sub>O<sub>3</sub> suspension batch was prepared, with 30 percent by volume solid material and a dispersing agent content of 2 percent by mass, relative to the powder mass. The layers were deposited from this suspension under the following conditions:

|  | with stirring  | without stirring |
|--|----------------|------------------|
| current  | 1000 $\mu$ A   | 1000 $\mu$ A     |
| total deposition time  | 11 hours 45min | 11 hours 45min   |
| d <sub>50</sub> in the suspension prior to the deposit             | 1.45 $\mu$ m   | 1.45 $\mu$ m     |
| d <sub>50</sub> in the suspension after 7 hours                    | 1.50 $\mu$ m   | 1.25 $\mu$ m     |
| d <sub>50</sub> in the suspension after 11h and 45min              | 1.61 $\mu$ m   | 0.51 $\mu$ m     |
| d <sub>50</sub> in the re-dispersed layer after 11 hours and 45min | 1.40 $\mu$ m   | 0.8 $\mu$ m      |

[00036] In each case, the distribution of particle sizes in the suspension was analyzed prior to, during, and after the deposition, as well as in the deposited layer following the re-dispersion in pure ethanol. The differential and cumulative distributions of particle sizes and the d<sub>50</sub> values for all measurements show that starting with a nearly symmetrical distribution of particle sizes with d<sub>50</sub> = 1.45 $\mu$ m and in clear contrast to the standard electrophoresis, the layer deposited with the method according to the invention has a noticeably reduced average value for the distribution of particle sizes as well as a clearly visible powder share with particle sizes below 500nm.

#### **Exemplary Embodiment 5:**

[00037] A PZT layer (lead-zirconate-titanate layer) was produced according to the invention by superimposing gravitational sedimentation on electrophoretic deposition. Counter electrode and substrate were arranged horizontally. To show that increasingly finer particles are deposited by means of the sedimentation, the peak-to-valley height was measured optically with the aid of a surface measuring device (FRT MicroGlider)

and based on DIN 4678 and/or ISO 4287. An additional layer was produced for comparison, for which the deposit by sedimentation was suppressed according to the prior art by stirring the suspension and for which the electrodes were arranged vertically.

A starting batch of an ethanol PZT suspension ( $d_{50} = 2.5\mu\text{m}$ ) was prepared, with 5 percent by volume solid material and a dispersing agent content of 2 percent by mass, relative to the powder mass. The layers were deposited from this suspension under the following conditions:

|                               | without stirring | with stirring<br>(200 rpm) |
|-------------------------------|------------------|----------------------------|
| electrode arrangement         | horizontal       | vertical                   |
| voltage                       | 5V               | 50V                        |
| average peak-to-valley height | 79nm             | 142nm                      |

[00038] The spacing between electrodes was 13mm. Respectively four profiles were analyzed in one layer and the average value listed. The result showed a clear reduction in the peak-to-valley depth of the layer with superimposed deposit by sedimentation.